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Project No.: 933-6154

August 18, 2006

Twinsburg, OH 44087

Ms. Valerie Orr
Ohio Environmental Protection Agency
Division of Drinking Water and Ground Water
Northwest District Office
2110 East Aurora Road

RE:

APPLICATION FOR AN EXEMPTION FROM FORMAL PERMITTING PROCEDURES FOR CLASS V 5X26 AQUIFER REMEDIATION PROJECTS NEASE CHEMICAL SITE, SALEM, OHIO

Dear Ms. Orr

Pursuant to an Administrative Order by Consent with the United States Environmental Protection Agency (USEPA) and as detailed in the Pre-Design Investigation Work Plan submitted to the Ohio Environmental Protection Agency (Ohio EPA) and the USEPA on May 25, 2006, RÜTGERS Organics Corporation (ROC) is required to conduct a short-term groundwater remediation field pilot injection test at the Nease Chemical Site referenced above. The pilot test is intended to evaluate the effectiveness of and define full-scale design parameters for an in-situ groundwater treatment process involving the injection of zero-valent nano scale iron through a well and into chemically impacted groundwater at the site.

The enclosed document provides ROC's application for an exemption from formal permitting procedures for Class V 5X26 Aquifer Remediation Projects. This document has been prepared in accordance with Ohio EPA's guidance entitled "5X26 Aquifer Remediation Projects".

If you have any questions regarding this application, please do not hesitate to contact us.

Very truly yours,

GOLDER ASSOCIATES INC.

P. Stephen Finn, C. Eng

Principal

PSF/bjb3:\projects\933-6154\ou-2 pdi workplan\work plan\uic form\uic application 8-18-06.doc

cc: Mr. Tim Christman, Ohio EPA

Ms. Sheila Abraham, Ohio EPA

Ms. Mary Logan, USEPA Dr. Rainer Domalski, ROC US EPA RECORDS CENTER REGION 5

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# APPLICATION 5X26 AQUIFER REMEDIATION PROJECT NEASE CHEMICAL SITE SALEM, OHIO

# Prepared for:

RÜTGERS Organics Corporation 201 Struble Road State College, PA 16801

## Prepared by:

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August 2006

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### 1.0 INTRODUCTION

Injection of fluids for the purposes of groundwater remediation field pilot testing is proposed to be performed in accordance with the Pre-Design Investigation Work Plan (PDI Work Plan) for Operable Unit Two (OU-2) at the Nease Chemical Site (Site) located in Salem, Ohio. The PDI Work Plan was submitted to the Ohio Environmental Protection Agency (Ohio EPA), care of Ms. Sheila Abraham, on May 25, 2006. The injection of fluids into groundwater, which was impacted from the former operation of two industrial wastewater treatment ponds, is to be performed during a short-term pilot testing phase of work as described in the PDI Work Plan and as summarized herein. This document is presented in support of an Application for an Exemption from formal Class V Well Permit to Install and Permit to Operate procedures and is developed in accordance with guidance for "5X26 Aquifer Remediation Projects" provided by the Ohio EPA.

This application is organized to present the nature of the source material affecting the pilot test area (Section 2.0), followed by relevant aspects of the site hydrogeology (Section 3.0), a description of the proposed remedial action and pilot testing (Section 4.0), and Ohio EPA reporting and oversight requirements (Section 5.0).

### 2.0 NATURE OF THE SOURCE MATERIAL

Former Ponds 1 and 2 are considered to be the primary source of groundwater impacts at the Site. Combined, former Ponds 1 and 2 cover approximately 1.5 acres, and are located adjacent to each other. The two former ponds lie directly upgradient of the pilot testing area as shown on the attached figures, which are Figure 3 and Figure 5 from the PDI Work Plan. Former Ponds 1 and 2 were historically used to neutralize chemical manufacturing wastewater during the former Nease Chemicals operations in the 1960s. These former ponds have since been backfilled following decommissioning of site operations.

Due to their close proximity and similar use, former Ponds 1 and 2 are addressed as a single area. Extensive soil data has been collected from test pits and soil borings installed within and/or adjacent to the former ponds during the remedial investigation (RI). A summary of the key soil information follows below.

- Total VOCs in soil ranged from 0.074 mg/kg to 53,519 mg/kg. The primary VOCs detected were tetrachloroethene (PCE), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), trichloroethene (TCE), and benzene; and,
- Total SVOCs in soil ranged from 0.084 mg/kg to 10,924 mg/kg. The primary SVOCs detected were diphenyl sulfone, hexachlorobenzene and 1,2-dichlorobenzene.

The analytical data from monitoring well PZ-6B-U that is screened in the upper portion of the Middle Kittaning Sandstone (MKS) unit directly downgradient of Former Ponds 1 and 2, are summarized below, based on the most recent (2003) sampling event:

- VOCs: 26 chemicals detected including chlorinated ethenes and ethanes, acetone, BTEX compounds, chlorinated benzene compounds, chloroform, methylene chloride, carbon disulfide, 1,2-Dichloropropane, styrene, naphthalene, and hexachlorobutadiene. The total VOC concentration measured was 165,065 ug/l; and,
- SVOCs: Hexachloroethane (4 J ug/l), 2,4-dichlorophenol (45 ug/l), 2,4,6-Trichlorophenol (8 J ug/l), and diphenyl sulfone (360 JN ug/l). The total SVOC concentration measured was 417 ug/l.

### 3.0 SITE HYDROGEOLOGY

In broad terms, the hydrogeologic units in the Site area consist of the following:

- Overburden (inclusive of fill, and silty/clay glacial till with discrete, discontinuous sand zones);
- Transition bedrock aquitard (Washingtonville Shale and associated coal seam and underclay); and,
- The MKS bedrock aquifer.

The overburden (glacial till), including the discrete, discontinuous sand zones, has an overall low net permeability and yields relatively low volumes of water. Although the sand horizons have an average hydraulic conductivity of about 10<sup>-4</sup> cm/sec, the silty clay portion which surrounds the sandy horizons in the glacial till displays hydraulic conductivities of about 10<sup>-7</sup> cm/sec, thus isolating the discrete sand seams within an aquitard, yielding little groundwater. The variably thick mantle of overburden overlies the surface of the Washingtonville Shale and associated coal seam and underclay that is broadly defined as the "transition zone aquitard". The MKS underlies the transition zone at the location of Former Ponds 1 and 2 (west of the Conrail right-of-way that bisects the Site), but is the uppermost bedrock unit east of the Conrail right-of-way where the Washingtonville Shale is mostly absent.

The proposed groundwater remediation pilot project focuses on testing in-situ treatment of groundwater within the MKS bedrock. Thus, the MKS groundwater hydraulics are further described below.

# MKS Bedrock Groundwater Flow Hydraulics

The predominant groundwater flow direction within the MKS is eastward (see attached Figure 5). Flow within the MKS occurs primarily through bedding plane partings. Flow can also occur across beddings planes when encountering a vertical joint. Groundwater velocity is variable within the MKS, typical of fractured bedrock systems. The groundwater flow velocity within the MKS is estimated to be 70-160 ft/yr. The average hydraulic conductivity of the MKS is 6.7x10<sup>-4</sup> cm/s.

### 4.0 DESCRIPTION OF PROPOSED REMEDIAL ACTION AND PILOT TESTING

### General Description of Technology

The MKS groundwater remedy selected for the Site, as described in the USEPA Record of Decision (ROD) for MKS groundwater, which was supported by Ohio EPA, includes in-situ groundwater treatment via the injection of nanoscale zero-valent iron (NZVI). In-situ NZVI treatment of groundwater is a relatively new technology that has been shown to be highly effective at treating a large variety of chemicals (through reduction pathways). Nanoscale iron particles, consisting of 1-100 nanometer sized particles of zero valent iron, provide rapid destruction of a wide range of chemicals based on an oxidation-reduction process where the chemical serves as an electron acceptor and NZVI as the electron donor. Chemicals such as trichloroethene (TCE), can accept electrons from ZVI and be reduced to non-toxic end products including ethene and ethane. Other compounds have also been shown to be treatable, such as trihalomethanes, chlorobenzene, PCBs and chlordane (Battelle, 2000). The reactivity of ZVI can be substantially enhanced by depositing a small amount (<1%) of a second metal (e.g., palladium).

The NZVI is introduced by injection as a slurry with water into a drilled well. Due to their small size, NZVI particles initially remain suspended in the groundwater flow. A relatively small groundwater mound is developed during injections, which dissipates rapidly after injection is completed. The suspended nano-scale iron particles will travel some distance from the injection well before the particles settle out. A diffuse reactive zone is formed around the injection point. Some particle remobilization may occur during subsequent injection events. With time, the iron particles will partially dissolve and their reactivity will decline. Greater penetration into the formation can be achieved through injection under pressure.

Treatment by NZVI has been shown to be immediately effective, and treatment potential is sustained for an extended period. Following treatment by NZVI, the groundwater will likely be in a highly reduced state, as dissolved oxygen will be eliminated, oxidation-reduction potential (ORP) will be greatly lowered, and pH will slightly increase.

### Description of Pilot Testing Procedures

Field pilot testing of NZVI treatment of groundwater will be performed using existing well PZ-6B-U as an injection well. Three new wells (NZVI-1/NZVI-2/NZVI-3) will be installed within

the MKS bedrock downgradient of PZ-6B-U at the locations shown on Figure 3 to monitor the effect of the injections. Wells NZVI-1 and NZVI-2 are located directly downgradient of the injection well, at close range (NZVI-1) and more distant (NZVI-2), while NZVI-3 is located off the estimated direct downgradient flow path at an intermediate distance. These wells will aid in evaluating the longitudinal and transverse extent of the influence of NZVI injections. The overall area of MKS groundwater pilot testing is limited to an area of approximately 25 feet by 50 feet downgradient of the injection well.

A slurry of NZVI<sup>1</sup> will be introduced into the injection well (PZ-6B-U) at relatively low pressure (approximately 30 pounds per square inch) over a period of two to three days. A potable source of water will be used to prepare the NZVI slurry. Groundwater may be extracted from downgradient well NZVI-2 to increase hydraulic gradients and facilitate the distribution of NZVI in the subsurface. The extracted groundwater will be treated at the on-site treatment plant prior to discharge. Based on Golder's experience at other sites, it is estimated that the injected slurry will contain 50 kg to 100 kg of NZVI suspended in 1,500 gallons to 2,500 gallons of water. The mass of NZVI and volume of water injected will be refined following the completion of a laboratory bench scale treatability study. Prior to the commencement of the field injection, Ohio EPA will be notified of the slurry quantities (i.e., NZVI and water) and type of NZVI that are proposed based on the results of the bench scale treatability study.

The NZVI-1 and -3 wells (and NZVI-2 if practicable) will be monitored continuously with downhole electronic dataloggers that will record potentiometric levels and selected geochemical parameters (dissolved oxygen, ORP, pH, specific conductance and temperature). Sampling for post-injection groundwater chemistry monitoring will be conducted periodically (1 week, 2 weeks, 4 weeks, 8 weeks, and 12 weeks) after the completion of NZVI injection. The frequency and duration of chemical monitoring may be adjusted depending on the results of the field study. Samples collected from all post-injection sampling events will be analyzed for the conventional full TCL volatile organics list (which includes chlorobenzene and dichlorobenzenes). An intermediate and the final post-injection sampling event will include analysis of VOCs, SVOCs and geochemical parameters in the same fashion as the Site baseline sampling event. The pilot

<sup>&</sup>lt;sup>1</sup> The slurry may consist of: NZVI produced by grinding ZVI powder manufactured by BASF to a size <100 nm or synthesizing palladized NZVI (bimetallic nanoscale particle (BNP)) to a size <100 nm, where the palladium acts as a catalyst. Additional information on ENP is provided in Attachment 1.

test monitoring is expected to be conducted for approximately three months. Further detailed field procedures for the NZVI field pilot test are included in the attached Appendix E.

### Well Installation and Development Procedures

The well drilling and installation will be performed by a driller licensed in the State of Ohio, and monitored by a Golder Associates geologist/engineer. Each NZVI well will be double-cased to minimize potential cross-contamination<sup>2</sup>. Each well will be constructed with 6-inch diameter steel casing installed approximately 5 feet into the MKS using hollow stem auger and air-rotary methods, and will be grouted and allowed to set overnight. The next phase of the boring will be completed by drilling within the 6-inch casing, using air-rotary methods, approximately 15 feet into the top of the MKS. During overburden drilling, head space analysis will be conducted on split spoon samples collected at 5-foot centers to the top of the MKS. The head space analysis will be performed using a calibrated photo-ionization detector (PID).

Each well will be completed using 2-inch ID, schedule 40 PVC casing and screen with water-tight Teflon-taped joints. The well screen length will be 15 feet for the NZVI wells.. The well screen intervals for the three monitoring wells will be placed such that the top of monitoring well screens will be approximately 2 feet above the top of the injection well (PZ-6B-U) screen and the base of the monitoring well screens 8 feet below the base of the injection well screen. This configuration allows monitoring of slightly deeper groundwater downgradient from the injection well. Consistent with these goals, the depth of the screen interval and the final well construction details will be determined in the field by the supervising geologist/engineer based on the local stratigraphy. The well screen slot size will be 0.010 inch (No. 10 slot). The well casings will extend from the top of the well screen to approximately 2 feet above the ground surface. A sand pack, comprised of clean, chemically non-reactive quartz sand will be placed around the well screen and will extend approximately 2 feet to 3 feet above the well screen. The sand pack material will be such that 90 percent by weight is larger than the screen slot size of 0.010 inch. A minimum of 1-foot of filter pack (fine-grained sand pack) will extend above the sand pack. No more than 5-feet of sand and filter pack (combined) will be used above the top of the well screen. A cement/bentonite grout (6 percent to 10 percent bentonite) mixture will then be placed using a tremie pipe (side discharge) from above the filter pack to the ground surface. A protective steel casing with a locking cap will be set

<sup>&</sup>lt;sup>2</sup> The construction of these wells will be consistent with the construction of existing well PZ-6B-U.

approximately 3 feet below ground surface (bgs) and will extend approximately 30 inches above ground surface.

After installation, each well will be developed by purging and surging in accordance with the Ohio EPA "Technical Guidance for Hydrogeologic Investigations and Ground Water Monitoring, Chapter 8, Ohio EPA, February 2004". Well development will not begin until the well seal has sufficiently cured and settled (generally within 48-hours). During development, water quality parameters (turbidity, pH, specific conductance) will be monitored and recorded and well development will continue until the parameters have stabilized. Development water will be containerized and will be temporarily stored on-Site pending disposal in the on-site treatment plant or shipped off-site for disposal.

5.0 AGENCY REPORTING AND OVERSIGHT

5.1 Reporting

Following completion of the pilot testing, a comprehensive report will be prepared and submitted to the USEPA, and to Ohio EPA, Division of Emergency and Remedial Response with a copy provided to the Division of Drinking and Ground Waters, UIC Unit.

5.2 Ohio EPA Oversight

Oversight by Ohio EPA will be coordinated by:

Ms. Sheila Abraham Division of Emergency and Remedial Response Northwest District Office 2110 East Aurora Road Twinsburg, OH 44087

Phone: 330-963-1290

# 6.0 REFERENCES

Battelle, 2000. Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation (Final). Study sponsored by SERDP, March 31, 2000.

# **ATTACHMENT 1**

# **Research Communications**

# Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs

CHUAN-BAO WANG AND WEI-XIAN ZHANG\*

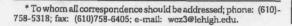
Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

Transformation of halogenated organic compounds (HOCs) by zero-valent iron represents one of the latest innovative technologies for environmental remediation. For example, iron can be used to construct a reactive wall in the path of a contaminated groundwater plume to degrade HOCs. In this paper, an efficient method of synthesizing nanoscale (1-100 nm) iron and palladized iron particles is presented. Nanoscale particles are characterized by high surface area to volume ratios and high reactivities. BET specific surface area of the synthesized metal particles is 33.5 m<sup>2</sup>/g. In comparison, a commercially available Fe powder (<10 μm) has a specific surface area of just 0.9 m<sup>2</sup>/g. Batch studies demonstrated that these nanoscale particles can quickly and completely dechlorinate several chlorinated aliphatic compounds and a mixture of PCBs at relatively low metal to solution ratio (2-5 g/100 mL). Surface-area-normalized rate constants (KsA) are calculated to be 10-100 times higher than those of commercially available iron particles. The approach presented offers unique opportunities for both fundamental research and technological applications of zero-valent metals. For example, a potential application of the nanoscale particles is to inject the metal particles directly into contaminated aquifers instead of building iron walls.

### Introduction

Destruction of halogenated organic compounds (HOCs) by zero-valent iron represents one of the latest innovative technologies for environmental remediation (I, Z). Laboratory research in the past few years has shown that granular iron can degrade many HOCs, including chlorinated aliphatics ( $\mathcal{J}$ ), chlorinated aromatics ( $\mathcal{J}$ ), and polychlorinated biphenyls (PCBs;  $\mathcal{J}$ ). Prospect for field application also looks promising. Granular iron can be adapted in the "funnel and gate" treatment system (I,  $\mathcal{J}$ ), in which a porous wall of granular iron is constructed in the path of a contaminated groundwater plume. As contaminated water passes through the reactive barrier, HOCs react with the surface of iron and form mostly benign compounds such as hydrocarbons, chloride, and water.

Implementation of the zero-valent iron technology still faces several challenges (7): (i) production and accumulation



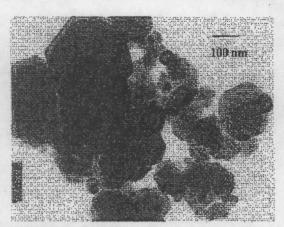


FIGURE 1. Transmission electron microscopy image of nanoscale Fe particles.

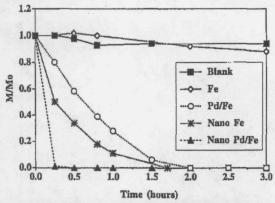


FIGURE 2. Reactions of TCE with commercial Fe powders (Fe), Pdmodified commercial Fe powders (Pd/Fe), nanoscale Fe particles (Nano Fe), and nanoscale Pd/Fe particles (nano Pd/Fe). Initial TCE concentration was 20 mg/L. Metal to solution ratio was 2 g/100 mL.

of chlorinated byproducts due to the low reactivity of iron powders toward lightly chlorinated hydrocarbons. For example, reduction of tetrachloroethene (PCE) and trichloroethene (TCE) by zero-valent iron has been observed to produce cis-1,2-dichloroethene (DCE) and vinyl chloride (VC; 3, 8). Both are of considerable toxicological concern; (ii) decrease of iron reactivity over time, probably due to the formation of surface passivation layers or due to the precipitation of metal hydroxides [e.g., Fe(OH)2, Fe(OH)3] and metal carbonates (e.g., FeCO3) on the surface of iron; (iii) engineering difficulties for constructing metal wall in deep aquifers (e.g., >30 m).

Many other metals, particularly zinc and tin, can transform HOCs more rapidly than iron (9). Palladium, with its catalytic ability, produces dramatic results as well. For example, recent studies have demonstrated that palladized iron can completely dechlorinate many chlorinated aliphatic compounds to hydrocarbons (10). The Pd/Fe bimetallic complexes have also been found to degrade PCBs with all the chlorines replaced by hydrogen to yield biphenyl (11).

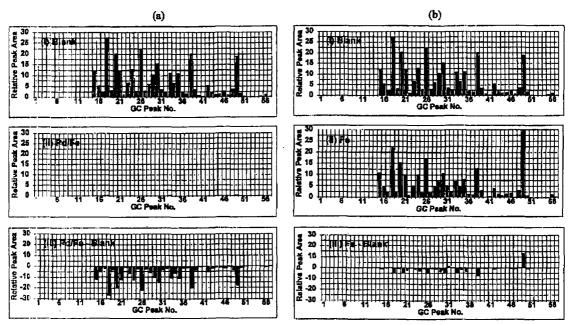


FIGURE 3. Changes in GC relative peak areas of an Aroclor 1254 solution in 17 h with (a) nanoscale Pd/Fe particles and (b) nanoscale Fe particles. GC peaks in (i) were from blank samples. Peaks in (ii) were from samples containing the nanoscale Fe or Pd/Fe particles. Peaks in (iii) were the difference between (ii) and (i) and represented the net degradation. Initial PCB concentration was 5 mg/L. Metal to solution ratio was 5 g/100 mL.

We report here an efficient method of synthesizing nanoscale iron and palladized iron particles and the results of using these metal particles for transformation of TCE and PCBs. Nanoscale metal particles, with diameter in the range of 1-100 nm ( $10^{-3}$  to  $10^{-7}$  m), are characterized by high surface area to volume ratios, high levels of stepped surface, and high surface energies (12, 13). Instead of building metal walls, nanoscale metal particles may be applied through direct injection of metal particle suspensions to contaminated sediments and aquifers (14). Freshly prepared metal particles free of surface contamination and with very high reactivities also provide ideal tools for elucidating fundamental mechanisms of dechlorination at the metal-solution interface. Furthermore nanoscale metal particles can be anchored on solid supports such as activated carbon, zeolite, and silica for ex-sitt, treatment of contaminated water and industrial effluent.

### **Experimental Methods**

Methods for Synthesis. Nanoscale Fe particles were produced by adding 1.6 M NaBH<sub>4</sub> (98%, Aldrich) aqueous solution dropwise to a 1.0 M FcCl<sub>3</sub>·6H<sub>2</sub>O (98%, Aldrich) aqueous solution at ambient temperature with magnetic stirring. Ferric iron (Fe<sup>2--</sup>) was reduced according to the following reaction (15):

Fe(H<sub>2</sub>D)<sub>6</sub><sup>3+</sup> + 3BH<sub>4</sub><sup>-</sup> + 3H<sub>2</sub>O 
$$\rightarrow$$
  
Fe<sup>0</sup>\(\daggered{\text{Fe}}\text{0}\daggered{\text{+}} 3B(OH)<sub>3</sub> + 10.5H<sub>2</sub> (1)

The wet Fe precipitates were coated with a thin layer of palladium by saturating the above precipitates with an ethanol solution of  $[Pd(C_2H_3O_2)_2]_3$  (47.5%, Alfa Aesar). This caused the reduction and subsequent deposition of Pd on the Fe surface through the following reaction (11):

$$Pd^{2+} + Fe^{0} \rightarrow Pd^{0} + Fe^{2+}$$
 (2)

Similar procedures were also employed to coat Pd on commercial iron powders (Aldrich, >99.9%, <10 µm).

Characterization of Synthesized Metal Particles. Surface areas (BET area) of the synthesized particles were measured using the nitrogen adsorption method with a Gemini 2360 surface analyzer. Prior to the measurements, dry Fe and Pd/ Fe particles were obtained by washing the wet precipitates with acetone and drying them at 110 °C for 6 h under a flow of N<sub>2</sub>. Morphology of the particles was observed with a Phillips EM 400T transmission electron microscopy (TEM) at 120 kV to characterize the size and size distribution of the metal particles. Crystal structures were examined with an APD 1700 automated powder X-ray diffractometer (XRD) with nickel-filtered CuKa radiation ( $\lambda = 0.1542$  nm).

Batch Experiments with TCE. Batch experiments were conducted to investigate reactivity of the synthesized particles for dechlorination of TCE. A 50-mL sample of 20 mg/L TCE aqueous solution and 1.0 g of the Fc or Pd/Fc particles were charged into a 50-mL serum bottle capped with a Teflon Mininert valve. The bottle was mixed on a rotary shaker (30 rpm) at ambient temperature (22 ± 1 °C). Parallel experiments were also performed without metal particles (blank) or commercial Fe powders (Aldrich, >99.9%, <10 µm). Periodically, 0.5 mL of the aqueous solution was withdrawn by a 1-mL gas-tight syringe into a 2-mL vial and extracted with 0.5 mL of pentane. Concentration of TCE was analyzed with a Hewlett-Packard Model 5890 GC equipped with an electron capture detector (ECD) and a BD-624 capillary column (Alltech Associates, Inc.). Hydrocarbon products in the headspace were identified with a Hewlett-Packard 5970 GC/MS.

Batch Experiments with PCBs. A 50-μL sample of 200 μg/mL Aroclor 1254 was combined with 0.1 g of the wet Fe or Pd/Fe particles and 2 mL of ethanol/water solution (volume ratio = 1:9), followed by mixing on a rotary shaker (30 rpm) for 17 h. Analytical methods were similar to those described above for TCE experiments. A 0.5-mL sample PCB solution was extracted by 0.5 mL of pentane and analyzed with GC-ECD.

#### Results

Figure 1 shows a transmission electron microscopy image of the synthesized Fe particles. More than 90% of the particles were in the size range of 1-100 nm. BET specific surface area of the particles was 33.5 m<sup>2</sup>/g. In comparison, a commercially available fine iron powder (Aldrich, >99.9%, <10 µm) has a specific surface area of about 0.9 m²/g, or 37 times less than that of the synthesized particles. XRD analysis further revealed the periodic lattice arrangement of iron atoms indicating crystalline structure of the nanoscale particles.

Degradation of TCE by various metal particles is presented in Figure 2. In all experiments, initial TCE concentration was 20 mg/L. Metal to solution ratio was 2 g/100 mL. The amounts of TCE in blank samples (without metal particles) and in the commercial Fe solution (Fe) remained relatively constant within a period of 3 h. TCE was completely dechlorinated by palladized commercial Fe powders (Pd/Fe) within 2 h, by the synthesized nanoscale Fe particles within 1.7 h, and by the synthesized nanoscale Pd/Fe bimetallic particles within less than 0.25 h (the soonest our measurement had been made). In the solutions containing the nanoscale particles, no chlorinated byproduct (i.e., DCEs, and VC) was detected. Final reaction products in the headspace of nanoscale particle solutions were identified to be hydrocarbons, including ethene, ethane, propenc, propane, butene, butana, and pentane.

Degradation of a PCB mixture (Aroclor 1254) solution by nanoscale Pd/Fe and Fe particles at ambient temperature (22 = 1 °C) is shown in Figure 3. Initial PCB concentration was 5 mg/L. Metal to solution ratio was 5 g/100 mL. GC peaks in (i) were from blank samples. Peaks in (ii) were from samples containing the nanoscale Fe or Pd/Fe particles. Peaks in (ii) were the difference between (ii) and (i) and represented the net degradation within 17 h. Few changes were observed for GC peaks in the blank samples over a period of 17 h (data not shown), indicating no natural degradation of PCBs in the absence of the metal particles. In the presence of synthesized nanoscale Pc/Fe particles (Figure 3a), GC pcaks disappeared completely within 17 h, suggesting complete dechlorination of PCB congeners of Aroclor 1254 by the nanoscale Pd/Fe particles at ambient temperature. In solution containing the nanoscale Fe particles (Figure 3b), only partial PCB reduction (<25% of the total mass) was observed within the same time perioc. Accumulation of biphenyl was confirmed by GC/MS in both solutions. In contrast, little degradation of PCBs was observed with the commercial iron powders under the same experimental conditions.

In summary, freshly synthesized nanoscale Fe particles were more reactive than the commercial Fe powders, likely due to the high specific surface area and higher surface reactivity. Surface-area-normalized rate constants (Ksa; 16) for the synthesized nanoscale particles (nano Fe) are calculatec to be  $3.0 \times 10^{-3}$  L hr<sup>-1</sup> m<sup>-2</sup>. In comparison, values of KsA for commercially available iron particles are generally below  $1.0 \times 10^{-3}$  L hr<sup>-1</sup> m<sup>-2</sup> (16). Nanoscale Pd/Fe bimetallic particles (nano Pd/Fe) were even more reactive than the pure Fe. KsA for the synthesized nanoscale Pd/Fe particles is about 0.1 L hr<sup>-1</sup> m<sup>-2</sup>, much higher than those of pure iron particles. Palladium could promote dechlorination reactions by serving as a catalyst accelerating the dissociation of chlorinated hydrocarbons (17). Palladium could also promote the dechlorination reactions by preventing the formation of iron oxides. Experiments have confirmed that the nanoscale Fe particles exposed to air reacted much more slowly with PCE and TCE than the freshly prepared iron particles. Addition of Pd onto Pe surface significantly reduced the oxidation of iron, thus preserving the reactivity of the zero-valent iron (17). We believe that the approach outlined here offers opportunities for both fundamental research and technological applications of zero-valent metals. Further studies are needed to delineate the underlying mechanistic steps of dechlorination on metal surfaces and to expand the scope of this synthesis method to other metals.

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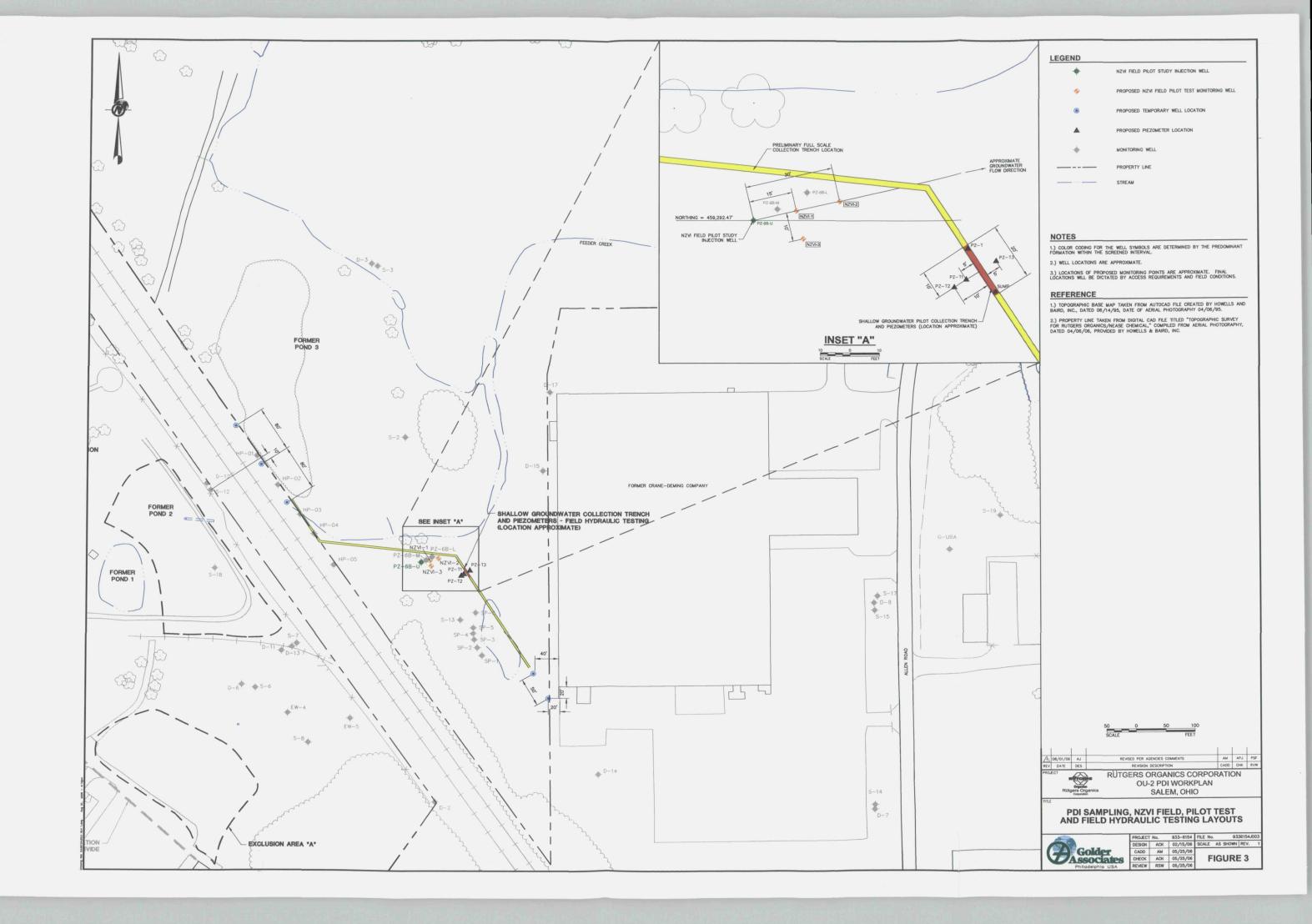
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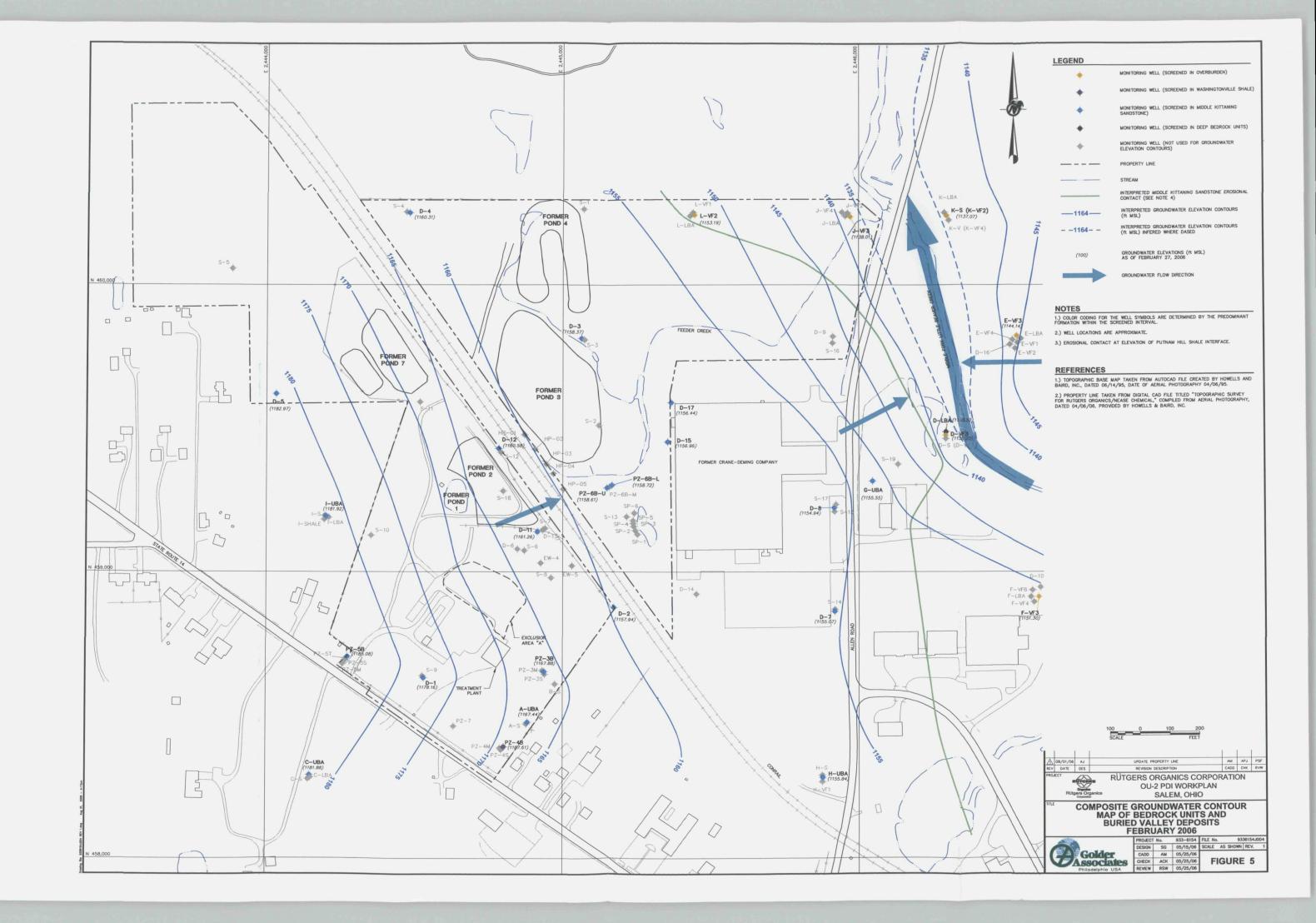
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# **ATTACHMENT 2**





# **ATTACHMENT 3**

### **NZVI FIELD TEST PROCEDURES**

### **Proposed Approach**

A pilot test is proposed using well PZ-6B-U as the NZVI injection well. New monitoring wells NZVI-1, NZVI-2 and NZVI-3 will be located as shown on Figure 3 of the PDI Work Plan. Implementation of the NZVI pilot test includes the following steps:

- 1. Conduct a round of baseline groundwater sampling;
- 2. Initiate in-situ groundwater treatment by pressure injection of a slurry of NZVI and water into existing monitoring well PZ-6B-U; and,
- 3. Conduct short-term and long-term monitoring of the effects of NZVI treatment through a combination of continuous field monitoring and collection of groundwater samples for laboratory analysis.

Following is a presentation of the proposed field activities outlined above. All the field work proposed in this work plan will be conducted in accordance with the procedures outlined in the PDI Work Plan.

### **Baseline Groundwater Sampling**

Baseline groundwater sampling of the NZVI field pilot testing wells will be conducted as part of the site wide baseline sampling event (see Section 3.1.2 of the PDI Work Plan main text). Analytes include VOCs, SVOCs, and geochemical parameters (see Table 1 of the PDI Work Plan).

### Baseline Hydraulic Testing

The new NZVI monitoring wells will be slug tested after installation and prior to commencement of NZVI field pilot testing activities. Existing wells PZ-6B-U/M/L will also be slug tested prior to the NZVI field test. This task will provide initial data to confirm the feasibility of injection into PZ-6B-U and assess the potential benefit of extraction from NZVI-2 and monitoring of adjacent wells.

### **Pump-in Test Implementation Procedures**

A pump-in test will be performed by injecting water from a potable water source<sup>1</sup> into PZ-6B-U. During injection, the flow rate and water level will be monitored in PZ-6B-U with an In-Situ TROLL<sup>TM</sup> transducer/datalogger. The test will include a short term step test followed by a 1.5-3 hour constant rate injection test. The step test will be conducted using different flow rates (steps) over a short period of time (e.g., 10 to 15 minutes). The flow rate for the constant rate test will be determined based on the step injection test. The constant rate test will be initiated following a recovery period of about 1.5-2 hours after the completion of the step test. The ideal constant injection rate will produce measurable responses (i.e., water level increases) in the observation wells without creating excessive mounding in the aquifer.

Water levels will be measured on a logarithmic scale, with ten minutes being the maximum interval. In addition, manual water level measurements will be recorded in the test well and observation wells at the beginning and end of the test, as a check on the transducer data.

Recovery of water levels in the test well will be measured for 1.5-3 hours on the same logarithmic scale following cessation of the pumping test. The recovery test data will also be used to determine the hydraulic conductivity of aquifer materials and will serve as verification of the pump-in test results.

### **NZVI** Injection

NZVI will be injected as a slurry suspension under low pressure. The NZVI will be transported to the site in a water solution in a 55-gallon drum. The NZVI solution will be pumped from the 55-gallon drum into a temporary holding tank and mixed with an on-site source of potable water to form the NZVI injection slurry. The NZVI slurry will be transferred from the holding tank to the injection well by an inline pump. The pressure maintained during injection will be approx mately 30 pounds per square inch. The total duration of the injection event is expected to be two to three days. In addition, groundwater may be extracted from downgradient well NZVI-2 to increase hydraulic gradient and facilitate the distribution of NZVI in the subsurface. The extracted groundwater will be treated at the on-site treatment plant prior to discharge. Flow rate and drawdown will be monitored in NZVI-2 during any groundwater extraction.

<sup>&</sup>lt;sup>1</sup> Prior to the pump-in test, a sample of the potable water source will be collected and analyzed for VOCs.

A total of three submersible pumps will be needed for the injection. The first submersible pump or alternatively, a mixer, will be placed in the holding tank to continuously recirculate and mix the slurry and maintain the NZVI particles in suspension. A second submersible pump will also be placed in the holding tank. The discharge of this pump will be connected to the injection well. The slurry will then be transferred to the well screen under the pressure generated by the pump. In-well mixing during injection may also be provided by the placement of a third submersible pump at the bottom of the injection well and equipping this pump with short discharge tubing (below the water level). This will allow for continuous recirculation of the NZVI slurry within the well screen area of the injection well. The recirculation pump will be operated until the iron is completely injected into the well. Following complete injection of the iron slurry into the well (which is expected to be conducted over a period of several days) the system will be operated for one additional hour using clean (potable) water, to allow for clearing of NZVI from the well bore.

The injection flow rate will be monitored with a totalizing flowmeter. Field indicator parameters specific conductance (SC), pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), temperature, and water level will be monitored with multiparameter Troll 9000 dataloggers set up in NZVI-1 and NZVI-3 beginning at least one day prior to NZVI injection. At the completion of injection, dataloggers will be installed in NZVI injection well PZ-6B-U and NZVI-2. A computer will be used in the field for programming of the dataloggers.

### **Post-Injection Groundwater Monitoring**

Post-injection monitoring of the effects of NZVI treatment will include groundwater sample collection for the analysis of geochemical parameters and VOC concentrations in both the injection and monitoring wells. Datalogger monitoring of selected geochemical parameters (dissolved oxygen, ORP, pH, specific conductance and temperature) will be carried out for a period of approximately one week following the completion of NZVI injection. Post-injection groundwater chemistry monitoring will be conducted as described in the main text of the PDI work plan. A summary of the pre- and post-injection monitoring program is shown on Table E-1.